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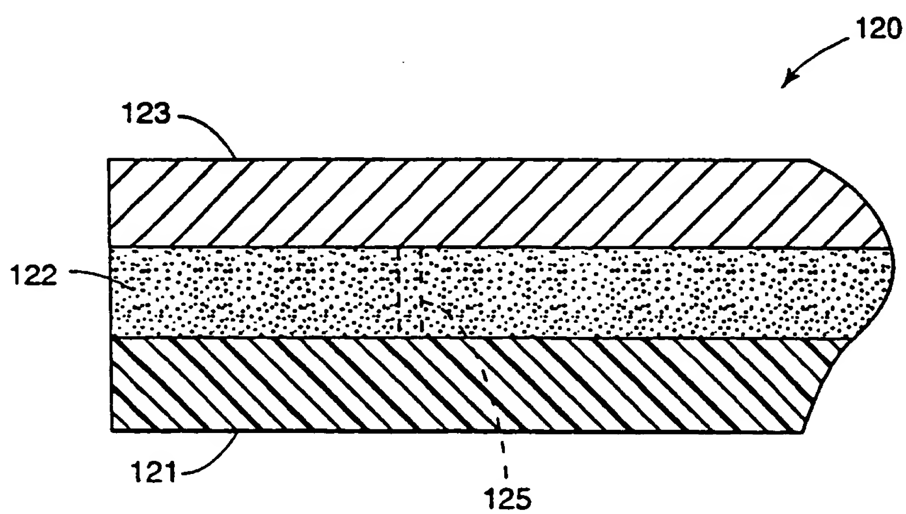
(54) Title: HOLOGRAPHIC PHOTOPOLYMER DATA RECORDING MEDIA AND METHOD OF HOLOGRAPHICALLY READING, RECORDING AND STORING DATA



(57) Abstract: A photopolymer data recording media including (i) a substrate layer, (ii) a capping layer, and (iii) a photopolymerizable layer between the substrate layer and the capping layer comprising (a) a highly branched, ethylenically unsaturated, cross-linkable, macromonomer having an average molecular weight of at least 2,000 and an ethylenically unsaturated group equivalent weight of less than 700, wherein neat macromonomer is flowable under ambient conditions, (b) an ethylenically unsaturated monomer, (c) a photosensitive initiator, and (d) optionally a sensitizer.

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HOLOGRAPHIC PHOTOPOLYMER DATA RECORDING MEDIA AND METHOD OF HOLOGRAPHICALLY READING, RECORDING AND STORING DATA

FIELD OF THE INVENTION

The invention relates to holographic data recording media and methods of holographically recording data onto and holographically reading data from such data recording media. More specifically, the invention relates to photopolymerizable holographic data recording media and methods of holographically recording data onto and holographically reading data from such data recording media.

BACKGROUND

Holographic data recording media permits data to be recorded at a density significantly greater than that achievable with conventional data recording media, such as magnetic data recording media.

Typical holographic data recording media comprises a photointeractive layer, such as photorefractive crystals or photosensitive polymers, sandwiched between a substrate layer and a capping layer. Data is recorded by directing interfering coherent reference and data light beams at a specific area on the surface of the holographic data recording media (*i.e.*, a page), with the photointeractive layer imaged with the data pattern of the data light beam. Reading is achieved by directing the reference beam at the specific page on the surface of the holographic data recording media and detecting the pattern of diffracted light passing through the media.

Photosensitive compositions suitable for use in the construction of holographic data recording media must possess certain properties and characteristics. The composition must be highly photosensitive and provide a high diffraction efficiency with low scattering and low shrinkage.

Typical photosensitive compositions include a polymeric binder, a photopolymerizable monomer, a photoinitiator and optionally a sensitizer. The various photosensitive compositions currently used in the construction of holographic data recording media possess these desired attributes to varying degrees. Accordingly, the search continues for photosensitive compositions possessing an improved combination of photosensitivity, diffraction efficiency, scattering and shrinkage for use in the construction of holographic data recording media.

SUMMARY OF THE INVENTION

We have discovered a photopolymer data recording media having a superior combination of high photosensitivity, high diffraction efficiency, low scattering and low shrinkage. The photopolymer data recording media includes (i) a substrate layer, (ii) a capping layer, and (iii) a photopolymerizable layer between the substrate layer and the capping layer. The photopolymerizable layer is comprised of a photopolymerizable composition including (a) a highly branched, ethylenically unsaturated, cross-linkable, macromonomer having an average molecular weight of at least 2,000 and an ethylenically unsaturated group equivalent weight of less than 700, wherein neat macromonomer is flowable under ambient conditions, (b) an ethylenically unsaturated monomer, (c) a photosensitive initiator, and (d) optionally a sensitizer.

We have further discovered a method for holographically imaging photopolymer data recording media, comprising the steps of (i) obtaining the photopolymer data recording media described above, (ii) creating an interference pattern by interfering a data beam and a reference beam, wherein the data beam contains an information pattern and the data beam and reference beam are comprised of electromagnetic radiation to which the photopolymerizable material is sensitive, and (iii) recording the interference pattern on the photopolymer data recording media in a pattern representative of the information pattern by exposing

the photopolymerizable material to the interference pattern for a time sufficient to effect photopolymerization of the photopolymerizable material.

We have still further discovered a method for reading a holographically imaged photopolymer data recording media, comprising the steps of (i) obtaining the photopolymer data recording media described above containing at least one recorded page of information recorded by differential interference pattern polymerization of the macromonomer and the monomer within pixels on the page so as to produce a page having pixels with different diffractive values, (ii) obliquely focusing a reference beam upon a selected page recorded on the data recording media, and (iii) detecting the presence or absence of the reference beam transmitted through the individual pixels of the page at a preselected angle of diffraction.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a schematic diagram of a standard holographic read, write and testing system.

Figure 2 is an enlarged cross-sectional side view of one embodiment of the holographic data recording media of the present invention.

DETAILED DESCRIPTION OF THE INVENTION INCLUDING A BEST MODE

Nomenclature

5	Typical Holographic Imaging Assembly
10i	Incident Beam
10t	Transmitted Beam
10d	Diffracted Beam
20	Output Beam
21p	Primary Beam
21r	Reference Beam

22	Expanded Primary Beam
23	Expanded Data Beam
24	Focused Data Beam
25	Reconstructed Data Beam
30	Source of Electromagnetic Radiation
40	HeNe Laser Source
50	Beam Splitter
60	Rotating Mirror
70	Mirror
80t	Transmitted Photodetector
80d	Diffracted Photodetector
90	Beam Expander
100	Spatial Light Modulator
110	Focusing System
120	Photopolymerizable Recording Media
121	Substrate
122	Photopolymerizable Layer
123	Capping Layer
125	Page on the Recording Media
130	Input Data Computer
140	CCD Detector Array
150	Output Data Computer
201	Input Data
202	Output Data

Definitions

As utilized herein, including the claims, the phrase ***"highly branched"***, when used to describe an organic molecule, means an organic molecule having at

least three carbon-containing branches extending from the backbone of the molecule with each branch having at least two carbon atoms.

As utilized herein, including the claims, the phrase ***"flowable"*** means the ability to assume the shape of a container.

As utilized herein, including the claims, the phrase ***"ambient conditions"*** means a temperature of 24°C ± 3°C and a pressure of 1 atmosphere ± 20%.

As utilized herein, including the claims, the phrase ***"primary branch"***, when used to describe a branch of an organic molecule, means a branch bonded directly to the backbone of the molecule.

As utilized herein, including the claims, the phrase ***"secondary branch"***, when used to describe a branch of an organic molecule, means a branch which is bonded to a primary branch and is not bonded directly to the backbone of the molecule.

As utilized herein, including the claims, the phrase ***"page"*** refers to an area of a data recording media upon which an individual information pattern (*e.g.*, array of differentially exposed pixels) can be recorded. A ***printed page*** is a page upon which an information pattern has been recorded (*e.g.*, exposure of selected pixels to an interference pattern). A ***blank page*** is a page upon which an information pattern has not been recorded.

As utilized herein, including the claims, the phrase ***"information pattern"*** means a pattern of differentially detectable pixels.

As utilized herein, including the claims, the phrase ***"pixel"*** means an individual cell of an array. An exemplary array is a standard tic-tac-toe board comprised of nine pixels.

Construction

Referring generally to Figure 2, the holographic data recording media **120** comprises a photopolymerizable layer **122** sandwiched between a substrate layer **121** and capping layer **123**.

SUBSTRATE AND CAPPING LAYERS

Materials suitable for use as the substrate layer **121** and capping layer **123** of the holographic data recording media **120** are well known and commercially available from a number of sources. Substantially any material having the necessary structural integrity may be employed so long as the material is transparent to the type of electromagnetic radiation to which the photopolymerizable material **120** is sensitive. Exemplary materials include specifically, but not exclusively, glass and plastic.

PHOTOPOLYMERIZABLE LAYER

The photopolymerizable layer **122** is the layer imaged with pages of information by patternwise exposing the layer to an interference pattern of electromagnetic radiation effective for photopolymerizing the photopolymerizable material. The photopolymerizable layer **122** is comprised of a photopolymerizable composition including an ethylenically unsaturated macromer, an ethylenically unsaturated monomer, a photoinitiator and optionally a sensitizer.

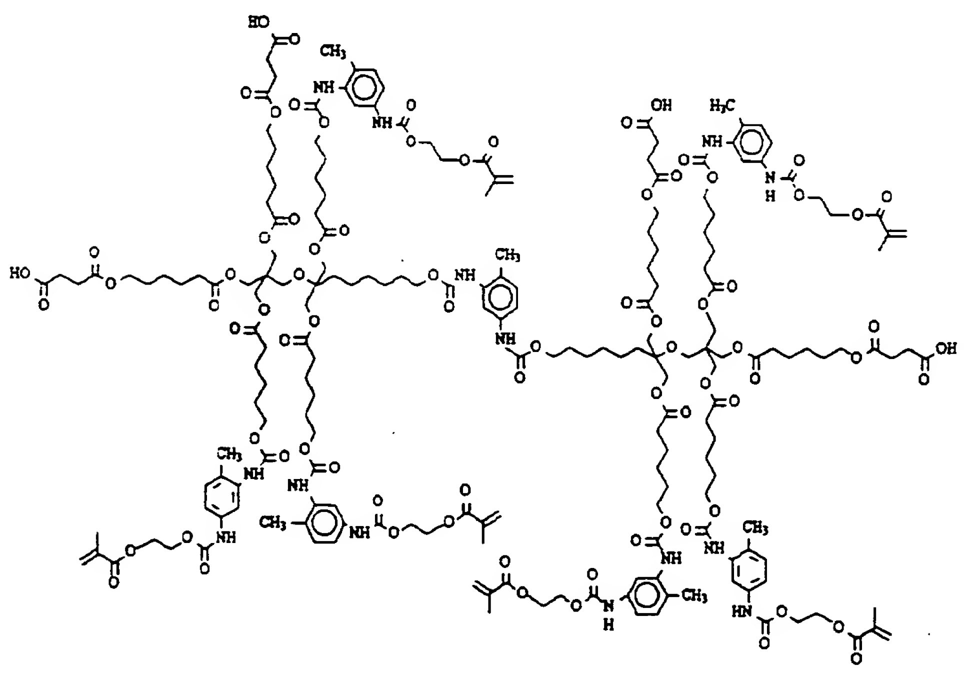
Macromer

The photopolymerizable composition includes a highly branched, ethylenically unsaturated, cross-linkable, macromonomer having an average molecular weight of at least 2,000, preferably 4,000, and an ethylenically unsaturated group equivalent weight of less than 700, preferably less than 500. Polymerization of such macromers solidifies the photosensitive composition with minimal shrinkage. The specified molecular weight, ethylenically unsaturated group equivalent weight and degree of branching each contribute to form a macromer which possesses the desired balance of flowability at ambient conditions in the absence of a solvent and minimal shrinkage when polymerized.

Preferred macromonomers have (i) at least four primary and/or secondary branches, and (ii) terminally positioned acrylate or methacrylate groups as the ethylenically unsaturated groups.

The neat macromonomer is sufficiently flowable under ambient conditions to permit the casting or coating of a relatively thick 1 to 3 mm layer between a substrate layer **121** and capping layer **123** without the formation of gas bubbles resulting from the entrapment of air) during coating/casting, or the introduction of a layer of air between the photosensitive composition and the substrate **121** and/or capping **123** layers, due to flow of the photosensitive composition after coating/casting.

A particularly suitable macromer is described in United States Letters Patent No. 4,228,232 (Preparation II) and Example 1 herein (hereinafter referenced as Macromer 1). The ideal structure of Macromer 1 is set forth below in Formula 1.



Formula 1

Briefly, Macromer 1 can be synthesized by (a) reactively combining dipentaerythritol with epsiloncaprolactone to form polycaprolactone hexol, (b) reactively combining the polycaprolactone hexol with 2,4-tolylene diisocyanate effective to form a first urethane as a first intermediate reaction product,, (c) reactively combining 2,4-tolylene diisocyanate and 2-hydroxyethylmethacrylate to form a second urethane as an intermediate reactant, (d) reactively combining the first urethane intermediate reaction product and the second urethane intermediate reactant to form a urethane oligomer as a second intermediate reaction product, and (e) reactively combining succinic anhydride and the urethane oligomer second intermediate reaction product to form the macromonomer.

The total amount of macromer present in the photopolymerizable layer **122** is from about 10 to about 80 wt% of the layer, more preferably between about 30 to 60 wt% of the layer.

Monomer

The photopolymerizable composition includes an ethylenically unsaturated monomer. Examples of suitable ethylenically unsaturated monomers and oligomers includes specifically, but not exclusively, (i) (meth)acrylic acid esters such as ethyl acrylate, butyl acrylate, and allyl acrylate; (ii) multifunctional acrylates and methacrylates such as zinc diacrylate, 1,6-hexanediol diacrylate, pentaerythritol triacrylate and tetraacrylate, 1,3,5-tri-(2-acryloyloxyethyl)isocyanurate, propoxylated glyceryl triacrylate, ethoxylated trimethylolpropane triacrylate, and polyethylene glycol dimethylacrylate; and (iii) derivatives of isocyanato containing ethylenically unsaturated compounds reacting with water, diols, polyols, dicarboxylic acids and polycarboxylic acids. Examples of the isocyanato monomers are 2-isocyanatoethyl methacrylate and dimethyl-m-isopropenyl benzyl isocyanate. An example of the reaction of an isocyanato containing ethylenically unsaturated compound with water is the reaction of 2-isocyanatoethyl methacrylate with water to form 1,3-bis(2'-

methyacryloxyethyl)urea (*e.g.*, CH_2=C(CH_3)-CO-OCH_2CH_2NH-CO-NHCH_2CH_2-CO-O-C(CH_3)=CH_2.

The total amount of ethylenically unsaturated monomers and/or oligomers present in the photopolymerizable layer **122** is from about 10 to about 90 wt% of the layer, more preferably between about 40 to 60 wt% of the layer.

Superior performance of the holographic recording media 120 can be obtained by utilizing a monomer having a refractive index which is substantially different than the refractive index of the macromer. Such a difference in the refractive indexes contributes to the ability of the media to diffract light passing through a printed page of the media.

Photoinitiators

The photopolymerizable composition includes a photoinitiator. The term "photoinitiator", as used herein, refers to any compound or combination of two or more compounds which, upon exposure to electromagnetic radiation, are capable of accelerating polymerization and crosslinking of the above described ethylenically unsaturated macromers, monomers and oligomers. Photoinitiators which initiate polymerization and crosslinking due to the production of free-radicals upon exposure to electromagnetic radiation are preferred. Preferred photoinitiators are active when exposed to radiation between 200 and 1200 nm (*e.g.*, ultraviolet, visible-light and infra-red radiation). Particularly preferred photoinitiators are active in the range of 300 to 850 nm.

Examples of suitable visible light and ultraviolet-induced photoinitiators include specifically, but not exclusively, (i) ketones such as benzils, benzoins, acyloins and acyloin ethers, such as 2,2,-dimethoxy-2-phenylacetophenone (Irgacure® 651), 2-benzyl-2-N,N-dimethylamino-1-(4-morpholinophenyl)-1-butanone (Irgacure® 369), and benzoin methyl ether (2-methoxy-2-phenylacetophenone), all commercially available from Ciba Specialty Chemicals Corp. of Tarrytown, New York; (ii) sensitized diaryliodonium salts and triarylsulfonium salts (described, for example, in United States Letters Patents.

Nos. 3,729,313; 4,058,400; 4,058,401; 4,460,154; and 4,921,827); (iii) sensitized arylalkyl borates commercially available from Ciba Specialty Chemicals Corp. of Tarrytown, New York, (iv) halomethyl-1,3,5-triazine compounds, such as those described in United States Letters Patent. No. 3,741,769; (v) chromophore-substituted halomethyl-1,3,5-triazine compounds, such as those described in United States Letters Patents. Nos. 3,987,037; 4,476,215; 4,826,753; 4,619,998; 4,696,888; 4,772,534; 4,189,323; 4,837,128; and 5,364,734, and (vi) halomethyl oxadiazoles such as those described in United States Letters Patents. No. 4,212,970. All such photoinitiators can be used alone or with suitable accelerators (*e.g.*, amines, peroxides, and phosphorous compounds) and/or with suitable sensitizers (*e.g.*, ketone or alpha-diketone compounds such as camphorquinone).

The photoinitiator is preferably present in the photosensitive layer in an amount sufficient to achieve the desired extent of polymerization. Such amount is dependent on the efficiency of the photoinitiator and the thickness of the photoactive layer. Typically a photoinitiator present in an amount of about 0.01 to 10 wt% of the photopolymerizable composition is effective. The preferred amount of photoinitiator is 0.5 to 8 wt% by weight of the coating and a particularly preferred amount being between 1 to 5 wt%.

Sensitizers

The photosensitive layer optionally but preferably includes an amount of a sensitizer effective for enhancing the photosensitivity of the photoinitiator. Any of the widely known and readily available sensitizers may be utilized, including specifically, but not exclusively, aryl nitrones, xanthenes, diphenylmethanes, xanthenes, acridines, methines, polymethines, thiazoles, thiazines, azines, aminoketones, porphyrins, colored aromatic polycyclic hydrocarbons, p-substituted aminostyryl compounds, amino methanes, anthraquinones, merocyanines, and squarylium compounds.

Method of Making

The photopolymerizable composition may be conveniently produced by simply blending together the macromer, monomer, photoinitiator and sensitizer in any desired order. Prior to casting, the composition should be dried to remove any residual solvent as the presence of any solvent tends to interfere with performance of the holographic data recording media **120**.

The photosensitive composition is positioned (e.g., cast or coated) between a substrate layer **121** and a capping layer **123** to form an intermediate photopolymerizable layer **122**. The photopolymerizable layer **122** may then be pre-cured to prevent the photopolymerizable layer **122** from flowing. An insufficiently pre-cured photopolymerizable layer **122** will tend to flow, resulting in a defective and unusable holographic data recording media **120**. An excessively pre-cured photopolymerizable layer **122** reduces the dynamic range available for the recording of holographic data (*i.e.*, a portion of the range of differentially detectable levels of polymerization is consumed by pre-curing of the photopolymerizable layer **122**).

The photopolymerizable layer **122** can have a thickness of between about 0.1 and 5 mm, with a thickness of about 0.25 and 3 mm preferred and a thickness of about 1 to 2 mm most preferred.

Method of Using

A typical holographic imaging and reading assembly **5** is depicted in Figure 1. For purposes of convenience, the assembly **5** shall first be described in connection with the holographic imaging of a photopolymerizable recording media **120**, and then in connection with the holographic reading of an imaged recording media **120**.

IMAGING

A source of electromagnetic radiation **30**, such as an argon ion laser, generates an output beam **20** of electromagnetic radiation. Prior to encountering the recording media **120**, the directed output beam **20** strikes a beam splitter **50** which splits the directed output beam **20** into a primary beam **21p** and a reference beam **21r**. The primary beam **21p** is expanded by a beam expander **90** and the expanded primary beam **22** reflected by mirror **70** into a spatial light modulator (SLM) **100**. The expanded primary beam **22** emerges from the SLM **100** as an expanded data beam **23**. The expanded data beam **23** is formed within the SLM **100** by the conventional process of superimposing a data array (not shown) upon the expanded primary beam **22**. The data array is generated within the SLM **100** based upon input data **201** received from a computer **130**. The data array causes the expanded primary beam **22** to define an array of "light" and "dark" pixels representative of the data received from the computer **130**. The expanded data beam **23** then passes through a focusing system **110**, with the focused data beam **24** brought into contact with the recording media **120**.

The reference beam **21r** is reflected by a rotating mirror **60** so as to cause the deflected reference beam **21r** to strike the same area of the recording media **120** as the focused data beam **24** at a desired angle of incidence. Such superimposed beams (*i.e.*, the focused data beam **24** and the deflected reference beam **21r**) interfere with one another resulting in the generation of an interference pattern in the recording media **120** within the "light" pixels and thereby creating the data array carried by the focused data beam **24**.

The type and intensity of the output beam **20** is selected so as to be effective for selectively polymerizing the polymerization layer **122** only in those areas corresponding to a "light" pixel of the interference pattern, while the "dark" pixels of the interference pattern are not appreciably polymerized. The polymerized and unpolymerized areas or pixels in the recording media **120** are characterized by different refractive indexes.

The imaging process is repeated for each page to be recorded on the recording media **120**, with a change in the physical location of the page on the recording media (*e.g.*, overlapped or individually positioned without overlap) and/or a change in the angle of incidence at which the reference beam strikes the recording media **120**.

READING

In order to read the data array imaged in the recording media **120**, the primary beam **21p** is blocked and only the reference beam **21r** is allowed to strike the page of the recording media **120** containing the data array at the same angle at which the data array was imaged. The reference beam **21r** is then diffracted by the data array imaged in the recording media **120** to generate a reconstructed data beam **25** along the same optical path as focused data beam **24**. Reconstructed data beam **25** contains the same array of "light" and "dark" pixels representative of the data array produced in the SLM **100**. Reconstructed data beam **25** then impinges on the CCD detector array **140** which converts the "light" and "dark" pixels into output data **202** for transmission to a computer **150**. Output data **202** is the same as input data **201** (*i.e.*, the original data stream output from the computer **130**).

The reading process is repeated for each page recorded on the recording media **120**, with a change in the physical location of the page on the recording media **120** (*e.g.*, overlapped or individually positioned without overlap) and/or a change in the angle of incidence at which the reference beam **21r** strikes the recording media **120**.

EXPERIMENTAL

GLOSSARY

Macromonomers

Macromer 1	A highly branched, ethylenically unsaturated, cross-linkable, macromonomer manufactured in accordance with the procedure set forth in United States Letters Patent No. 4,228,232 (Preparation II) and Example 1 herein, and having the ideal structure set forth in Formula 1 herein.

Monomers

BAEDA	Bisphenol A ethoxylate (1 EO/phenol) diacrylate available from Aldrich Chemical Company of Milwaukee, Wisconsin.
BAEDMA	Bisphenol A ethoxylate (2 EO/phenol) dimethacrylate available from Aldrich Chemical Company of Milwaukee, Wisconsin.
BAGDA	Bisphenol A glycidyl diacrylate available from Polysciences, Inc. of Warrington, Pennsylvania.

BPEA	2-(2-Bromophenyl)ethyl acrylate prepared from 2-(2-bromophenyl)ethanol and acrylol chloride, both available from Aldrich Chemical Company of Milwaukee, Wisconsin.
CEA	2-Cyanoethyl acrylate available from Aldrich Chemical Company of Milwaukee, Wisconsin.
CPA	4-Cyanophenyl acrylate prepared from 4-Cyanophenol and acryloyl chloride, both available from Aldrich Chemical Company of Milwaukee, Wisconsin.
CPEA	2-(2-Cyanophenyl)ethyl acrylate prepared from 2-Cyanophenol, available from Aldrich Chemical Company of Milwaukee, Wisconsin, and 2-Bromoethyl acrylate, available from Polysciences, Inc. of Warrington, Pennsylvania, in acetone in the presence of potassium carbonate.
DCHQDA	2,3-Dicyanohydroquinone diacrylate synthesized from 2,3-Dicyanohydroquinone and Acryloyl chloride, both available from Aldrich Chemical Company of Milwaukee, Wisconsin.
EGPA	2-Phenoxyethyl acrylate available from Aldrich Chemical Company of Milwaukee, Wisconsin.

NA	2-Naphthyl acrylate prepared from 2-naphthol and acryloyl chloride, both available from Aldrich Chemical Company of Milwaukee, Wisconsin.
PEOMA	Polyethyleneoxide methacrylate having n EO units per methacrylate group wherein n is approximately 10 available from Polysciences, Inc. of Warrington, Pennsylvania.
Initiators	
BTPB	Butyltriphenyl borate available from Ciba Specialty Chemicals Corp. of Tarrytown, New York.
EDMAB	Ethyl-4-dimethylamino benzoate available from Aldrich Chemical Company of Milwaukee, Wisconsin.
TTT	2,4,6-Tris-trichloromethyl-1,3,5-triazine available from Aldrich Chemical Company of Milwaukee, Wisconsin.
Sensitizers	
CQ	Camphorquinone available from Aldrich Chemical Company of Milwaukee, Wisconsin.
Safranine-O	Safranine-O available from Aldrich Chemical Company of Milwaukee, Wisconsin.

TESTING PHOTOPOLYMERIZABLE RECORDING MEDIA

Referring to Figure 1, for the purposes of testing photopolymerizable recording media, the computers **130** and **150**, the beam expander **90**, the SLM **100**, the CCD detector **140**, and the data streams **201** and **202** are removed from the assembly **5**. An argon ion laser **30**, generates an output beam **20** of electromagnetic radiation. Prior to encountering the recording media **120**, the directed output beam **20** strikes a beam splitter **50** which splits the directed output beam **20** into a primary beam **21p** and a reference beam **21r**. The power of radiation in each of the primary beam **21p** and reference beam **21r** is independently measured by introducing photodetectors (not shown) into the optical path of each beam. The primary beam **21p** is reflected by mirror **70** through focusing system **110** onto the recording media **120**. The reference beam **21r** is simultaneously reflected by mirror **60** onto the same area of the recording media **120** as the primary beam **21p** to generate an interference pattern of light and dark stripes. The light stripes cause polymerization within the photosensitive media, whereas the dark stripes cause little or no polymerization, thereby producing a diffraction pattern of differing refractive indexes.

A HeNe laser **40**, is used to measure the diffraction efficiency and light scatter of the diffraction pattern produced in the photopolymerizable recording media **120** by the reference beam **21r** and primary beam **21p**. The laser **40** generates an incident beam **10i** which strikes the same area of **120** as beams **21r** and **21p**. The power of the incident beam **10i** can be measured by introducing a photodetector (not shown) into the optical path of **10i**. The incident beam **10i** passes through the media **120** before it is imaged to produce a transmitted beam **10t**, the power of which is determined by photodetector **80t**. Once a diffraction pattern is produced in the recording media **120** by beams **21r** and **21p**, the incident beam **10i** is diffracted at its Bragg angle to produce a diffracted beam **10d**, the power of which is determined by photodetector **80d**.

Example 1
(Synthesis of Macromer 1)

Into a 500 ml three-neck flask fitted with an overhead mechanical stirrer and a condenser was placed 63.5 grams dipentaerythritol, 228 grams epsiloncaprolactone and 0.02 grams 2,6-di-t-butyl-4-methyl phenol to form a first reaction mixture. The first reaction mixture was deoxygenated for 20 minutes by bubbling the mixture with dry nitrogen from a gas dispersion tube. The tube was replaced with a gas inlet adapter and the first reaction mixture heated while maintaining a slight positive pressure with nitrogen. The first reaction mixture was maintained at 70°C for 5 hours under continuous stirring to form a polycaprolactone hexol mixture. The polycaprolactone hexol mixture was then allowed to cool to room temperature under a nitrogen atmosphere.

Into a 1000 ml three-neck flask fitted with an adapter, mechanical stirrer, thermometer, addition funnel and drying tube was placed 175 grams of the polycaprolactone hexol mixture and 60 ml of methylethyl ketone to form a diluted polycaprolactone hexol mixture. Into the diluted polycaprolactone hexol mixture was slowly dripped, at room temperature and under constant agitation, a solution of 13 grams of 2,4-tolylene diisocyanate in 9 ml of methylethyl ketone to form a second reaction mixture. The addition was completed over a 20 minute period and the second reaction mixture stirred for 90 minutes at 30°C to form a first intermediate mixture, at which time infrared spectroscopy indicated that essentially all of the 2,4-tolylene diisocyanate had reacted.

A separate flask fitted with an overhead mechanical stirrer, thermometer, addition funnel and drying tube was charged with 86.1 grams of 2,4-tolylene diisocyanate. The addition funnel was charged with 70.2 grams of 2-hydroxyethylmethacrylate (HEMA) and 0.02 grams 2,6-di-t-butyl-4-methyl phenol. The HEMA was slowly added under constant agitation to the 2,4-tolylene diisocyanate while maintaining the temperature at or below 30°C to form a third reaction mixture. The addition was completed over a 15 minute period and the third reaction mixture stirred for 40 minutes, at which time a white solid reaction product had formed. The solid reaction product was dissolved in 45 ml of

methylethyl ketone by heating to 45 °C, and the resultant solution held at that temperature for 10 minutes to form a second intermediate mixture.

The flask containing the first intermediate mixture was heated to 67 °C and the second intermediate mixture was added slowly over a two hour period with constant stirring to form a fourth reaction mixture. Into the fourth reaction mixture was then added 27 grams of succinic anhydride and 0.02 grams 2,6-di-t-butyl-4-methyl phenol to form a fifth reaction mixture. The fifth reaction mixture was then maintained at 67 °C and under constant agitation until the reaction had run to completion (approximately 5 to 6 hours) to from the urethane oligomer (hereinafter "Macromer 1") whose ideal structure is represented by Formula 1.

Example 2
(Construction and Testing of Holographic Data Recording Media)

Sample photopolymerizable compositions were made by blending together a macromer, monomer, initiator(s) and sensitizer as listed in Table One at room temperature, followed by drying of the composition under high vacuum to remove any residual solvent. The dry photopolymerizable composition was then cast between two glass disks separated by a polycarbonate spacer so as to form a holographic data recording media having a cast layer of photopolymerizable composition with a thickness as set forth in Table One. The cast layer of photopolymerizable composition was then pre-cured with a Minnesota Mining and Manufacturing Company Model 70 tungsten lamp for the time period set forth in Table One to set the layer of photopolymerizable composition and form a completed holographic data recording media.

The diffraction efficiency (DE) and scattering value (SV) of the completed holographic data recording media were tested with the holographic sensitivity testing system described previously herein. Testing of the completed holographic data recording media was effected at the exposure conditions set forth in Table Two. The Diffraction Efficiency (DE) and Scattering Value (SV) of the media were then calculated in accordance with the Diffraction Efficiency and Scattering

Value Formulas set forth below wherein the Diffraction Efficiency of Experiments C1-C5 and 1-9 and 12-44 were calculated in accordance with DE^1 and the Diffraction Efficiency of Experiments 10 and 11 were calculated in accordance with DE^2. The Scattering Value of Experiments C1-C2, 1-5 and 10-11 were subjectively determined by positioning a white substrate behind the completed holographic data recording media and visually determining the sharpness of the beam as an indication of the extent of scattering on a relative scale of No Scattering, Very Little Scattering, Little Scattering, Small Scattering, Moderate Scattering, and High Scattering. Test results and calculated values are set forth in Table Two.

$$DE^1 = (\text{Diffraction}) / (\text{Incident})$$

$$DE^2 = (\text{Diffraction}) / [(\text{Diffraction}) + (\text{Transmitted})]$$

$$SV = 1-[(\text{Diffraction}) - (\text{Transmitted})] / (\text{Incident})$$

wherein Diffraction, Transmitted and Incident refer to the power of the diffracted, transmitted and Incident laser beams, respectively.

TABLE ONE

Composition #	Composition: Macromonomer Type	Macromonomer wt%	Monomer Type	Monomer wt%	Initiator/Sensitizer Type	Initiator/Sensitizer wt%	Thickness (mm)	Precure Time (sec)
C1	---	---	BAEDMA CEA	47.5 47.5	EDMAB TTT CQ	2 2 1	2	20
C2	---	---	BAGDA CEA	47.5 47.5	EDMAB TTT CQ	2 2 1	2	30
C3	---	---	BAGDA CEA	47.5 47.5	EDMAB TTT CQ	2 2 1	2	20
1	Macromer 1	38	CEA	56	EDMAB TTT CQ	2 2 1	2	20-30

Composition	COMPOSITION						Thickness	Precure Time
	Macromonomer		Monomer		Initiator/Sensitizer			
#	Type	wt%	Type	wt%	Type	wt%	(mm)	(sec)
2	Macromer 1	47.5	CEA	47.5	EDMAB TTT CQ	2 2 1	2	20
3	Macromer 1	47	BAEDA CPA	36 12	EDMAB TTT CQ	2 2 1	1	30-40
4	Macromer 1	41.5	BAEDA DCHQDA	41.5 10	EDMAB TTT CQ	2 2 1	1	40-60
5	Macromer 1	41	BAEDA DCHQDA	41 14	EDMAB TTT CQ	2 2 1	1	50-60
6	Macromer 1	31.6	BAEDA BPEA	31.7 31.7	EDMAB TTT CQ	2 2 1	0.25	100

Composition	COMPOSITION						Thickness	Precure Time
	Macromonomer		Monomer		Initiator/Sensitizer			
#	*Type*	*wt%*	*Type*	*wt%*	*Type*	*wt%*	*(mm)*	*(sec)*
7	Macromer 1	31.6	BAEDA BPEA	31.6 31.6	EDMAB TTT CQ	2 2 1	1	100
8	Macromer 1	31.6	BAEDA BPEA	31.6 31.6	EDMAB TTT CQ	2 2 1	1	120
9	Macromer 1	31.6	BAEDA BPEA	31.6 31.6	EDMAB TTT CQ	2 2 1	1	140
10	Macromer 1	54	BAGDA	41	EDMAB TTT CQ	2 2 1	2	10
11	Macromer 1	54	BAGDA	41	EDMAB TTT CQ	2 2 1	2	20

Composition	COMPOSITION						Thickness	Precure Time
	Macromonomer		Monomer		Initiator/Sensitizer			
#	*Type*	*wt%*	*Type*	*wt%*	*Type*	*wt%*	*(mm)*	*(sec)*
12	Macromer 1	47.5	BAEDA	47.5	EDMAB TTT CQ	2 2 1	0.25	10
13	Macromer 1	47.5	BAEDA	47.5	EDMAB TTT CQ	2 2 1	0.25	15
14	Macromer 1	47.5	BAEDA	47.5	EDMAB TTT CQ	2 2 1	2	20
15	Macromer 1	47.5	BAEDA	47.5	EDMAB TTT CQ	2 2 1	2	25
16	Macromer 1	47.5	BAEDA	47.5	EDMAB TTT CQ	2 2 1	2	35

Composition	Composition						Thickness	Precure Time
	Macromonomer		Monomer		Initiator/Sensitizer			
#	*Type*	*wt%*	*Type*	*wt%*	*Type*	*wt%*	*(mm)*	*(sec)*
17	Macromer 1	41.3	BAEDA NMA	41.3 12.4	EDMAB TTT CQ	2 2 1	1	30
18	Macromer 1	41.3	BAEDA NMA	41.3 12.4	EDMAB TTT CQ	2 2 1	1	40
19	Macromer 1	41.3	BAEDA NMA	41.3 12.4	EDMAB TTT CQ	2 2 1	1	50
20	Macromer 1	47	BAEDA NMA	24 24	EDMAB TTT CQ	2 2 1	1	50
21	Macromer 1	47	BAEDA NMA	24 24	EDMAB TTT CQ	2 2 1	1	60

Composition	COMPOSITION						Thickness	Precure Time
	Macromonomer		Monomer		Initiator/Sensitizer			
#	*Type*	*wt%*	*Type*	*wt%*	*Type*	*wt%*	*(mm)*	*(sec)*
22	Macrome r 1	47	BAEDA NMA	24 24	EDMAB TTT CQ	2 2 1	0.25	10
23	Macrome r 1	49	BAEDA	49	BTPB Safranine-O	2 0.018	0.2	2-4
24	Macrome r 1	49	BAEDA	49	BTPB Safranine-O	2 0.018	0.2	2

TABLE TWO

Experiment	Composition	Writing Conditions			Diffraction Efficiency	Scattering Value
		Power	Wavelength	Time		
#	#	(mW)	(nm)	(msec)		
C1	C1	30	488	10-100	High	Moderate
C2	C2	30	488	500-1,000	Little	Little
C3	C3	30	488	5	14	---
C4	C3	30	488	10	23	---
C5	C3	30	488	30	40	---
1	1	30	488	10-200	Good	Very Low
2	2	30	488	3-200	15-25†	Little
3	3	30	488	5-100	15-33†	Little
4	4	30	488	10-300	17-69†	Little
5	5	30	488	10-100	12-65†	Small
6	6	15	488	20-200	15-39†	---
7	7	15	488	10-200	25-47†	---

Experiment	Composition	Writing Conditions			Diffraction Efficiency	Scattering Value
		Power	Wavelength	Time		
#	#	(mW)	(nm)	(msec)		
8	8	15	488	5-20	43-69†	---
9	9	15	488	10-40	54-59†	---
10	10	30	488	5-100	50-78†	High
11	11	30	488	10-50	15-35†	Little
12	12	30	488	3	5.8	12.7
13	12	30	488	100	15.1	16.5
14	13	30	488	10	5.1	13.5
15	13	30	488	100	13.7	14.6
16	14	30	488	5	31.5	19.9
17	14	30	488	100	54.8	25.4
18	15	30	488	3	37.3	15.6
19	15	30	488	10	43.8	15.4
20	16	30	488	3	23.6	12.8
21	16	30	488	10	28.1	12.1

Experiment	Composition	Writing Conditions			Diffraction Efficiency	Scattering Value
		Power	Wavelength	Time		
#	#	(mW)	(nm)	(msec)		
22	16	30	488	100	56.1	13.1
23	17	30	488	3	35.4	15.1
24	11_1	30	488	10	38	16.7
25	17	30	488	20	41.7	19.6
26	18	30	488	3	50.1	15.8
27	19	30	488	3	8.0	15.0
28	19	30	488	10	45.4	16.1
29	19	30	488	50	48.5	14.7
30	19	30	488	100	50.9	17.4
31	20	30	488	5	24.2	14.3
32	20	30	488	20	47.6	13.9
33	20	30	488	50	46.7	14.2
34	20	30	488	200	34.1	15.0
35	21	30	488	5	21.8	14.2

Experiment	Composition	Writing Conditions			Diffraction Efficiency	Scattering Value
		Power	Wavelength	Time		
#	#	(mW)	(nm)	(msec)		
36	21	30	488	20	43.6	14.1
37	21	30	488	50	47.8	15.0
38	21	30	488	200	37.7	14.6
39	22	30	488	5	2.2	14.3
40	22	30	488	10	15.4	12.9
41	22	30	488	50	12.8	12.7
42	22	30	488	100	12.5	12.6
43	23	3	532	10-1000	10-25†	---
44	24	3	532	10-1000	15-30†	---

† DE observed over range of writing times specified in the example.

Conclusion: Good DE with acceptable SV can be achieved with holographic data recording media of the present claimed invention.

We Claim:

1. A photopolymer data recording media for holographic imaging and data storage, comprising:
   (a) a substrate layer,
   (b) a capping layer, and
   (c) a photopolymerizable layer between the substrate layer and the capping layer, the photopolymerizable layer comprising a photopolymerizable material including at least:
      (1) a highly branched, ethylenically unsaturated, cross-linkable, macromonomer having an average molecular weight of at least 2,000 and an ethylenically unsaturated group equivalent weight of less than 700, wherein neat macromonomer is flowable under ambient conditions,
      (2) an ethylenically unsaturated monomer,
      (3) a photosensitive initiator, and
      (4) optionally a sensitizer.

2. The photopolymer data recording media of claim 1 wherein the substrate layer and capping layer are individually comprised of glass or plastic which is transparent to that electromagnetic radiation to which the photopolymerizable material is sensitive.

3. The photopolymer data recording media of claim 1 wherein the photopolymerizable material includes at least:
   (a) about 30 to 60 wt% macromonomer,
   (b) about 40 to 60 wt% monomer
   (c) an effective amount of photosensitive initiator, and
   (d) an effective amount of a sensitizer.

4. The photopolymer data recording media of claim 1 wherein the ethylenically unsaturated groups on the macromonomer are terminally positioned acrylate or methacrylate groups.

5. The photopolymer data recording media of claim 4 wherein the macromonomer has an average of at least four combined primary and secondary branches.

6. The photopolymer data recording media of claim 4 wherein the macromonomer is the product formed by:
   (a) reactively combining dipentaerythritol with epsiloncaprolactone to form polycaprolactone hexol,
   (b) reactively combining the polycaprolactone hexol with 2,4-tolylene diisocyanate effective to form a first urethane as a first intermediate reaction product,
   (c) reactively combining 2,4-tolylene diisocyanate and 2-hydroxyethylmethacrylate to form a second urethane as an intermediate reactant,
   (d) reactively combining the first urethane intermediate reaction product and the second urethane intermediate reactant to form a urethane oligomer as a second intermediate reaction product, and
   (e) reactively combining succinic anhydride and the urethane oligomer second intermediate reaction product to form the macromonomer.

7. The photopolymer data recording media of claim 1 wherein the macromonomer has an average molecular weight of at least 4,000.

8. The photopolymer data recording media of claim 1 wherein the monomer is selected from the group consisting of EGPA, PEOMA, BAEDMA, BAEDA, CEA, CPA, CPEA, DCHQDA, BPEA and NA.

9. A method for holographically imaging a photopolymer data recording media, comprising:

(a) obtaining a photopolymer data recording media, according to any one of claims 1-8,

(b) creating an interference pattern by interfering a data beam and a reference beam, wherein the data beam contains an information pattern and the data beam and reference beam are comprised of electromagnetic radiation to which the photopolymerizable material is sensitive, and

(c) recording the interference pattern on the photopolymer data recording media in a pattern representative of the information pattern by exposing the photopolymerizable material to the interference pattern for a time sufficient to effect photopolymerization of the photopolymerizable material.

10. A method for holographically reading a holographically imaged photopolymer data recording media, comprising:

(a) obtaining a holographically imaged photopolymer data recording media according to any one of claims 1-8, wherein the photopolymerizable layer includes at least one recorded page of information recorded by differential interference pattern polymerization of the macromonomer and the monomer within pixels on the page so as to produce a page having pixels with different diffractive values,

(b) obliquely focusing a reference beam upon a selected page recorded on the data recording media, and

(c) detecting presence or absence of the reference beam transmitted through the individual pixels of the page at a preselected angle of diffraction.

Fig. 1

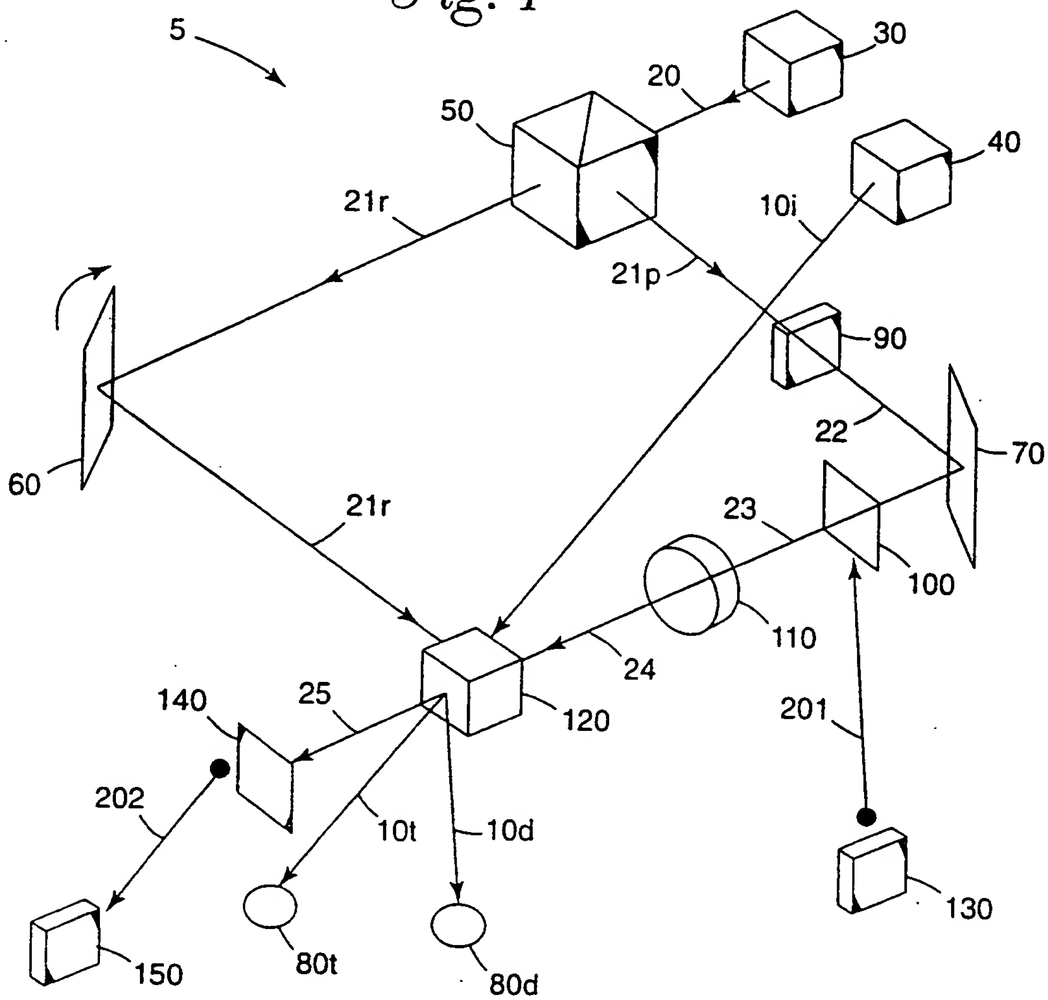
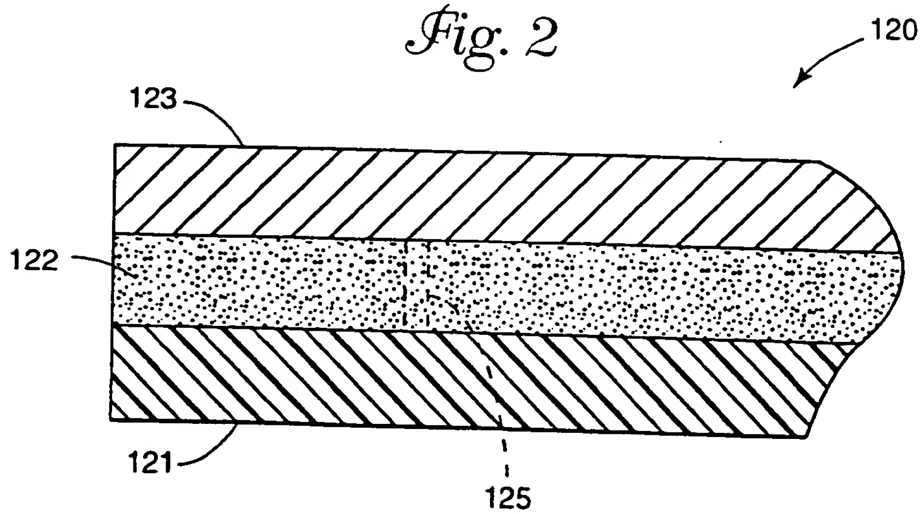

5
30
20
50
40
21r
10i
21p
90
22
70
60
21r
23
100
110
24
201
140
25
120
202
10t
10d
130
150
80t
80d

Fig. 2


120
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INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 00/01679

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 G03F7/027 G03F7/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 G03F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 304 923 A (A.D. ROUSSEAU) 8 December 1981 (1981-12-08) cited in the application column 10, line 46 - line 68 column 11, line 1 - line 35	1,3-7
Y	column 18; example 16	2,8
Y	EP 0 824 222 A (LUCENT TECHNOLOGIES INC.) 18 February 1998 (1998-02-18) page 4, column 6, line 32 - line 33 page 5, column 7, line 51 - line 53 figure 1	2,8
A	EP 0 530 613 A (AGFA-GEVAERT AG) 10 March 1993 (1993-03-10) page 6 -page 8	1-10

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

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"P" document published prior to the international filing date but later than the priority date claimed

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
29 May 2000	07/06/2000

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Dupart, J.-M.

1

International Application No
PCT/US 00/01679

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
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